Consommation et Corporations Canada
Bureau des [redacted]ts
Ottawa, Canada
K1A 0C9

Consumer and Corporate Affairs Canada
Patent Office

(21) (A1) 2,068,328
(22) 1990/11/07
(43) 1991/05/10

5,025,2/51

(51) INTL.CL.[5] C07D-401/04; A01N-043/54

(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Pyrimidine Derivatives, Process for Making Them, Agents Containing Them and Their Use as Fungicides

(72) Giencke, Wolfgang - Germany (Federal Republic of) ;
Sachse, Burkhard - Germany (Federal Republic of) ;
Wicke, Heinrich - Germany (Federal Republic of) ;

(73) Hoechst Aktiengesellschaft - Germany (Federal Republic of) ;

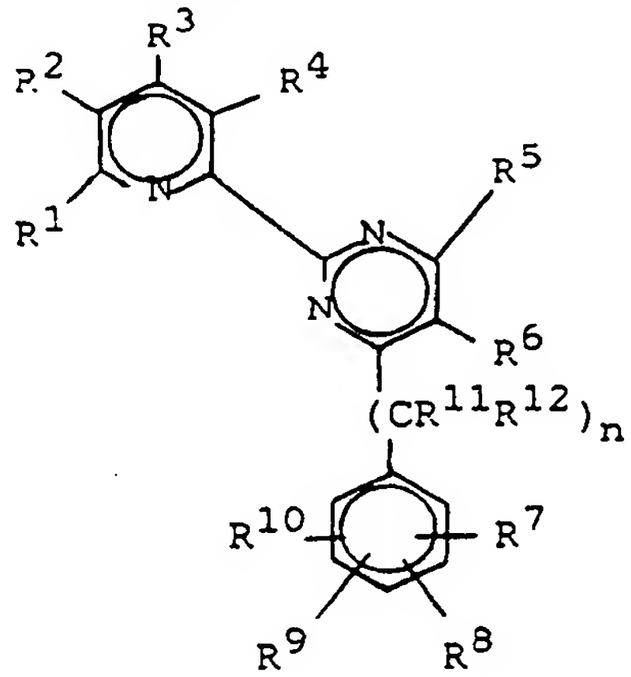
(30) (DE) P 39 37 284.7 1989/11/09

(57) 6 Claims

Abstract of the disclosure

Pyrimidine derivatives, process for their preparation, agents containing them and their use as fungicides

Compounds of the formula I



(I)

in which

R^1 is hydrogen, alkyl, alkoxyalkyl, alkylthioalkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, it being possible for the two last-mentioned radicals to be substituted in the cycloalkyl moiety, phenyl, phenoxyalkyl, phenylmercaptoalkyl, phenylalkyl or phenoxy-phenoxyalkyl, it being possible for this radical to be substituted in the phenyl moiety,

R^2, R^3 and R^4 are independently of one another hydrogen, alkyl or (subst.) phenyl,

R^5 is hydrogen, alkyl, cycloalkyl, cycloalkylalkyl, it being possible for these two radicals to be substituted in the cycloalkyl moiety, haloalkyl, alkoxy, alkylthio, alkoxyalkyl, alkylthioalkyl, halogen, alkenyl, alkynyl, phenyl, phenoxy, phenylalkyl, phenoxyalkyl, phenylmercaptoalkyl, phenylmercapto, phenylalkoxy or phenylalkylthio, it being possible for these radicals to be substituted in the phenyl moiety, or alkenyloxy, alkynyloxy, haloalkoxy, alkoxyalkoxy or alkylthioalkylthio,

R^6 is hydrogen, alkyl, alkoxy, alkenyloxy,

alkynyloxy, alkylthio, halogen, phenyl, it being possible for the phenyl radical to be substituted,

R^7, R^8, R^9 and R^{10} are independently of one another hydrogen, halogen, nitro, cyano, alkyl, alkoxy, alkylthio, haloalkyl or haloalkoxy,

R^{11} and R^{12} are independently of one another hydrogen or alkyl and

n = 1-3, and their acid addition salts have advantageous fungicidal properties.

HOECHST AKTIENGESELLSCHAFT HOE 89/F 360 Dr. VP/PP

Description

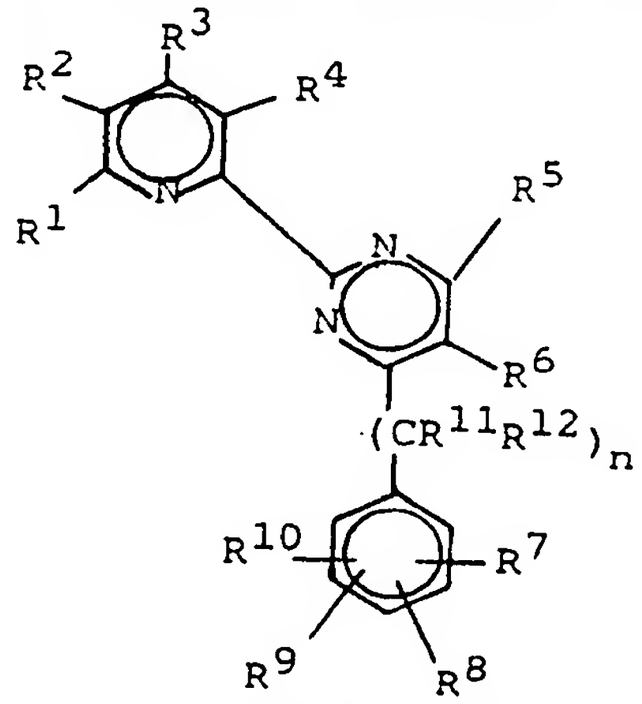
Pyrimidine derivatives, process for their preparation, agents containing them and their use as fungicides

The present invention relates to novel pyrimidine derivatives, a process for their preparation, agents containing them and their use as fungicides.

Pyrimidine derivatives are already known as active components in fungicidal agents (cf. EP-A-270,362, EP-A-259,139, EP-A 234,104). However, the action of these compounds is not always satisfactory, in particular at low application rates.

Novel pyrimidine derivatives have now been found which have advantageous effects in the control of a wide spectrum of phytopathogenic fungi, in particular at low dosages.

The present invention therefore relates to the compounds of the formula I,



(I)

in which

R^1 is hydrogen, (C_1-C_6)alkyl, (C_1-C_4)alkoxy-(C_1-C_4)-alkyl, (C_1-C_4)alkylthio-(C_1-C_4)alkyl, (C_2-C_6)alkenyl, (C_2-C_6)alkynyl, (C_3-C_7)cycloalkyl, (C_3-C_7)-cycloalkyl(C_1-C_4)alkyl, it being possible for the two last-mentioned radicals to be monosubstituted

to trisubstituted in the cycloalkyl moiety by (C_1-C_4)alkyl, or phenyl, phenoxy-(C_1-C_4)alkyl, phenylmercapto(C_1-C_4)alkyl, phenyl-(C_1-C_4)alkyl or phenoxy-phenoxy(C_1-C_4)alkyl, it being possible for the five last-mentioned radicals to be monosubstituted to trisubstituted in the phenyl moiety by halogen, nitro, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl or (C_1-C_4)haloalkoxy,

R^2, R^3 and R^4 are independently of one another hydrogen, (C_1-C_6)alkyl or phenyl, it being possible for the phenyl radical to be monosubstituted to trisubstituted by halogen, nitro, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1 -C_4)haloalkyl, or (C_1-C_4)haloalkoxy,

R^5 is hydrogen, (C_1-C_6)alkyl, (C_3-C_7)cycloalkyl, (C_3-C_7)cycloalkyl-(C_1-C_4)alkyl, it being possible for the two last-mentioned radicals to be monosubstituted to trisubstituted in the cycloalkyl moiety by (C_1-C_4)alkyl, (C_1-C_4)haloalkyl, (C_1-C_4)-alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)alkoxy-(C_1-C_4)-alkyl, (C_1-C_4)alkylthio-(C_1-C_4)alkyl, halogen, (C_2-C_6)alkenyl, (C_2-C_6)alkynyl, phenyl, phenoxy, phenyl(C_1-C_4)alkyl, phenoxy-(C_1-C_4)alkyl, phenyl-mercapto-(C_1-C_4)alkyl, phenylmercapto, phenyl-(C_1-C_4)alkoxy or phenyl-(C_1-C_4)alkylthio, it being possible for the eight last-mentioned radicals to be monosubstituted to trisubstituted in the phenyl moiety by halogen, nitro, cyano, (C_1-C_4)-alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)halo-alkyl or (C_1-C_4)haloalkoxy, or (C_2-C_4)alkenyloxy, (C_2-C_4)alkynyloxy, (C_1-C_4)haloalkoxy, (C_1-C_4)alkoxy-(C_1-C_4)alkoxy or (C_1-C_4)alkylthio-(C_1-C_4)alkylthio,

R^6 is hydrogen, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_2-C_6)-alkenyloxy, (C_2-C_6)alkynyloxy, (C_1-C_4)alkylthio, halogen or phenyl, it being possible for the phenyl radical to be monosubstituted to trisubstituted by halogen, nitro, cyano, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl or

(C_1-C_4)haloalkoxy,

R^7, R^8, R^9 and R^{10} are independently of one another hydrogen, halogen, nitro, cyano, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl or (C_1-C_4)haloalkoxy,

R^{11} and R^{12} are independently of one another hydrogen or (C_1-C_4)alkyl and

n is 1-3, and their acid addition salts.

The alkyl, alkenyl or alkynyl radicals here can be both straight-chain and branched. Halogen is F, Cl, Br and I, preferably F, Cl and Br. The prefix "halo" in the description of a substituent here and in the following means that this substituent can occur once or several times with the same or a different meaning. The prefix "halo" comprises fluorine, chlorine, bromine or iodine, in particular fluorine, chlorine or bromine. Examples of haloalkyl which may be mentioned are: CF_3, CF_2CHF_2, CF_2CF_3, CCl_3, CCl_2F, $CF_2CF_2CF_3$, CF_2CHFCF_3 and $(CF_2)_3CF_3$. Examples of haloalkoxy are OCF_3, OCF_2CHF_2 or $OCF_2CF_2CF_3$.

Preferred compounds of the formula I are those in which

R^1 is hydrogen, (C_1-C_6)alkyl, phenyl, phenyl-(C_1-C_2)-alkyl, phenoxy-phenoxy-(C_1-C_2)alkyl or phenoxy-(C_1-C_2)alkyl, it being possible for the four last-mentioned radicals to be monosubstituted to trisubstituted in the phenyl moiety by halogen or (C_1-C_4)alkyl; or (C_1-C_3)alkoxy-(C_1-C_2)alkyl,

R^2 and R^3 are independently of one another hydrogen, (C_1-C_3)alkyl or phenyl, it being possible for the phenyl radical to be monosubstituted to trisubstituted by halogen or (C_1-C_4)alkyl,

R^4 is hydrogen,

R^5 is hydrogen, (C_1-C_6)alkyl, (C_3-C_6)cycloalkyl, (C_5-C_6)cycloalkyl-(C_1-C_3)alkyl, phenyl, phenyl-(C_1-C_2)alkylthio, phenyl-(C_1-C_2)alkyl, it being possible for the three last-mentioned radicals to be monosubstituted to trisubstituted in the

phenyl moiety by halogen, (C_1-C_4)alkyl, (C_1-C_3)-haloalkyl or (C_1-C_4)alkoxy, or (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_2-C_4)alkenyloxy, (C_2-C_4)alkynyloxy, (C_2-C_3)alkenyl, (C_2-C_4)alkynyl or (C_1-C_4)alkoxy-(C_1-C_4)alkoxy,

R^6 is hydrogen, (C_1-C_4)alkyl, halogen, phenyl or (C_1-C_3)alkoxy,

R^7, R^8, R^9 and R^{10} are independently of one another hydrogen, (C_1-C_4)alkyl, (C_1-C_4)haloalkyl or (C_1-C_4)-alkylthio,

R^{11} and R^{12} are hydrogen,

and n = 1, and their acid addition salts.

The following acids are suitable for the preparation of the acid addition salts of the compounds of the formula I:

hydrohalic acid such as hydrochloric acid or hydrobromic acid, and in addition phosphoric acid, nitric acid, sulfuric acid, mono- or bifunctional carboxylic acids and hydroxycarboxylic acids such as acetic acid, maleic acid, succinic acid, fumaric acid, tartaric acid, citric acid, salicylic acid, sorbic acid or lactic acid, and sulfonic acids such as p-toluenesulfonic acid or 1,5-naphthalene-disulfonic acid. The acid addition salts of the compounds of the formula I can be obtained in a simple manner by customary salt formation methods, for example by dissolving a compound of the formula I in a suitable organic solvent and adding the acid and are isolated in a known manner, for example by filtering off, and, if desired, purified by washing with an inert organic solvent.

The present invention also relates to a process for the preparation of the compounds of the formula I.

The novel pyrimidine derivatives of the formula (I) can be prepared by the following methods:

1) Pyrimidine derivatives of the formula I where R^5 = H can be obtained by reductive dehalogenation of

appropriate halopyrimidines of the formula I in which R^5 is halogen (Cl, Br, or I) and the remaining substituents are as defined in formula I. The dehalogenation can be carried out with hydrogen in the presence of catalysts (for example palladium/carbon) in an inert solvent, for example water, lower alcohol (such as methanol and ethanol), ethyl acetate or toluene or mixtures thereof. The addition of bases such as alkali metal hydroxides or alkali metal carbonates or alkaline earth metal hydroxides or alkaline earth metal carbonates is advantageous. The reaction is carried out in the range 15-60°C under a pressure of 1 to 5 bar.

2) Pyrimidine derivatives of the formula I, in which R^5 is (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, phenoxy, phenylmercapto, phenyl-(C_1-C_4)alkoxy or phenyl-(C_1-C_4)alkylthio, it being possible for the 4 last-mentioned radicals in the phenyl moiety to be monosubstituted to trisubstituted by halogen, nitro, cyano, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-_4)haloalkyl or (C_1-C_4)haloalkoxy, or (C_2-C_4)alkenyloxy, (C_2-C_4)alkynyloxy, (C_1-C_4)haloalkoxy, (C_1-C_4)alkoxy-(C_1-C_4)alkoxy or (C_1-C_4)alkylthio-(C_1-C_4)alkylthio, can be prepared by reaction of the appropriate halopyrimidines of the formula (I) R^5 = halogen with an alkali metal compound of the formula where R^5-Y (II), in which R^5 has the abovementioned meaning and Y is an alkali metal. Examples of alkali metal are sodium, potassium and lithium.

The reaction can be carried out between 0°C and 130°C in the course of 0.5 h to 72 h. The alkali metal compound (II) can be employed in amounts of 1 to 2 mol equivalents relative to 1 equivalent of the halopyrimidine (I). The reaction is usually carried out in the presence of a solvent.

In the cases in which an alkali metal compound R^5-Y

is employed in which R^5 is (C_1-C_4)alkoxy, (C_2-C_4)-alkenyloxy, (C_2-C_4)alkynyloxy, (C_1-C_4)haloalkoxy or (C_1-C_4)alkoxy-(C_1-C_4)alkoxy, the corresponding alcohol R^5OH or an ether (for example diethyl ether, dioxane or tetrahydrofuran) or a mixture thereof is expediently used as the solvent. In the cases in which an alkali metal compound R^5Y is employed in which R^5 is (C_1-C_4)alkylthio, phenoxy, phenylmercapto, phenyl-(C_1-C_4)alkoxy, phenyl-(C_1-C_4)alkylthio or (C_1-C_4)-alkylthio-(C_1-C_4)alkylthio, an ether (for example diethyl ether, dioxane or tetrahydrofuran), a nitrile (for example acetonitrile), an aromatic hydrocarbon (for example toluene or xylene) or a mixture thereof is used as the solvent.

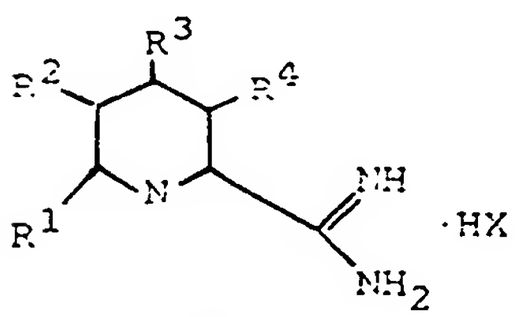
3) Pyrimidine derivatives of the formula (I), in which R^5 is (C_1-C_6)alkyl, (C_3-C_7)cycloalkyl, (C_3-C_7)cycloalkyl-(C_1-C_4)alkyl, (C_1-C_4)alkoxy-(C_1-C_4)alkyl, (C_1-C_4)alkylthio-(C_1-C_4)alkyl or phenyl, it being possible for the last-mentioned radical to be monosubstituted to trisubstituted by (C_1-C_4)alkyl or (C_1-C_4)-alkoxy, can be obtained by reaction of appropriate halopyrimidines of the formula (I) where R^5 = halogen with Grignard compounds R^5MgX (III), where R^5 is defined as indicated above and X is halogen (Cl, Br or I), in the presence of nickel-phosphine complexes such as, for example, 1,2-bis(diphenylphosphino)-ethane-nickel(II) chloride or 1,3-bis(diphenylphosphino)propane-nickel(II) chloride (cf. Chem. Pharm. Bull. 16, 2160 (1978)). The reaction can be carried out in the course of 2 - 48 h between 0°C and 80°C or at the boiling point of the solvent. The Grignard compound R^5MgX (III) can be employed in amounts of 1-2.5 mol equivalents relative to 1 equivalent of halopyrimidine (I). Suitable solvents are ethers such as, for example, diethyl ether, THF, dioxane and dimethoxyethane.

The halopyrimidines I (R^5 = halogen) can be obtained

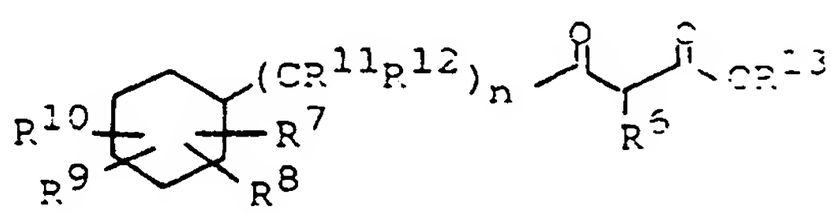
by reaction of the appropriate hydroxypyrimidines I (R^5 = OH), in which R^1-R^4, R^6-R^{12} and n are as defined as in the general formula (I), with halogenating agents. Halogenating agents which can be employed are, for example, thionyl chloride, phosgene, phosphorus oxychloride, phosphorus pentachloride, phosphorus oxybromide or phosphorus tribromide. The reactions can be carried out in a solvent, but also without solvent.

The halogenating agent is employed in amounts of 1 to 4 equivalents relative to 1 equivalent of the hydroxypyrimidine (I). The reactions can be carried out in a temperature range from 25 to 160°C. Solvents employed are, for example, aromatic hydrocarbons (for example benzene or toluene, inter alia) or halogenated hydrocarbons (for example chlorobenzene).

The hydroxypyrimidines (I) can be prepared by condensation of the amidine derivatives (IV) with β-oxocarboxylates (V)



IV



V

in which R^1-R^4, R^6-R^{12} and n are as defined in formula I, X is halogen (for example chlorine, bromine or iodine) and R^{13} is lower alkyl radicals such as methyl, ethyl and propyl.

The reactions are carried out in the temperature

range from 20 to 110°C or at the boiling point of the solvent within the course of 2 - 72 h. The β-oxocarboxylate V can be employed in amounts of 1 - 1.5 equivalents relative to 1 equivalent of amidine derivative IV. The reaction is carried out in the presence of a base and of a solvent. Bases employed can be, for example, inorganic bases such as alkali metal hydroxides and carbonates or organic bases such as sodium alkoxides, trialkylamines and N,N-dialkylanilines. Suitable solvents are lower alcohols (such as methanol and ethanol), cyclic ethers (such as dioxane and THF), pyridine, N,N-dimethylformamide, water or mixtures thereof.

The amidine derivatives IV and the β-oxocarboxylates V can be prepared by processes known per se (cf. J. Org. Chem. 32, 1591 (1967) and Synthesis 1982, 451 and Organikum 1986, 516 et seq.).

The compounds of the formula I according to the invention are distinguished by an excellent fungicidal action. Causative organisms of fungal disease which have already penetrated into the plant tissue can be successfully controlled in a curative manner. This is particularly important and advantageous in those fungal diseases which, after infection has occurred, can no longer be controlled effectively with the otherwise customary fungicides. The spectrum of action of the compounds claimed includes a plurality of various economically important phytopathogenic fungi, such as, for example, Piricularia oryzae, Venturia inaequalis, Cercospora beticola, powdery mildew species, Fusarium species, Plasmopora viticola, Pseudoperonospra cubensis [sic], Leptosphaeria nodorum, Drechslera, various rust fungi and Pseudocercosporella herpotrichoides. Benzimidazole- and dicarboximide- sensitive and -resistant Boytritis cinerea [sic] strains are particularly well controlled.

The compounds according to the invention are in addition

also suitable for use in industrial fields, for example as wood preservatives, as preservatives in paints, in cooling lubricants for metal processing or as preservatives in drilling and cutting oils.

The invention also relates to agents which contain the compounds of the formula I in addition to suitable formulation auxiliaries.

The agents according to the invention in general contain the active compounds of the formula I in amounts of 1 to 95% by weight.

They can be variously formulated, depending on how it is prespecified by the biological and/or physicochemical parameters. Suitable formulation possibilities are therefore:
wettable powders (WP), emulsifiable concentrates (EC), aqueous solutions (SC), emulsions, sprayable solutions, dispersions having an oil or water base (SC), suspo-emulsions (SC), dusting agents (DP), seed dressings, granules in the form of micro-, spray, absorption and adsorption granules, water-dispersible granules (WG), ULV formulations, microcapsules, waxes or baits.

These individual formulation types are known in principle and are described, for example, in: Winnacker-Küchler, "Chemische Technologie" (Chemical Technology), Volume 7, C-Hauser Verlag Munich, 4th Ed. 1986; van Falkenberg, "Pesticides Formulations", Marcel Dekker N.Y., 2nd Ed. 1972-73; K. Martens, "Spray Drying Handbook", 3rd Ed. 1979, G. Goodwin Ltd. London.

The formulation auxiliaries required such as inert materials, surfactants, solvents and other additives are likewise known and are described, for example, in: Watkins, "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Darland Books, Caldwell N.J.; H.v. Olphen, "Introduction to Clay Colloid Chemistry", 2nd

Ed., J. Wiley & Sons, N.Y.; Marschen [sic], "Solvents Guide", 2nd Ed., Interscience, N.Y. 1950; McCutcheon's, "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridgewood N.J.; Sisley and Wood, "Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; Schönfeldt, "Grenzflächenaktive Äthylenoxidaddukte" (Surface-active ethylene oxide adducts), Wiss. Verlagsgesell., Stuttgart 1976; Winnacker-Küchler, "Chemische Technologie" (Chemical Technology), Volume 7, C. Hauser Verlag Munich, 4th Ed. 1986.

On the basis of these formulations, combinations with other pesticidally active substances, fertilizers and/or growth regulators can also be prepared, for example in the form of a finished formulation or as a tank mix.

Wettable powders are preparations which can be uniformly dispersed in water and, apart from the active compound and a diluent or inert substance, additionally contain wetting agents, for example polyoxyethylated alkylphenols, polyoxyethylated fatty alcohols, alkyl- or alkylphenolsulfonates and dispersing agents, for example sodium ligninsulfonate, sodium 2,2'-dinaphthylmethane-6,6'-disulfonate, sodium dibutylnaphthalenesulfonate or, alternatively, sodium oleylmethyltaurate. Emulsifiable concentrates are prepared by dissolving the active compound in an organic solvent, for example butanol, cyclohexanone, dimethylformamide, xylene or, alternatively, higher-boiling aromatics or hydrocarbons with the addition of one or more emulsifiers. Examples of emulsifiers which can be used are:

alkylarylsulfonic acid calcium salts such as Ca dodecylbenzenesulfonate or nonionic emulsifiers such as fatty acid polyglycol esters, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, propylene oxide-ethylene oxide [lacuna] sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters or polyoxyethylene sorbitol esters.

Dusting agents are obtained by grinding the active compound with finely divided solid substances, for example talc, natural clays such as kaolin, bentonite, poryphillite [sic] or diatomaceous earth. Granules can either be prepared by spraying the active compound onto adsorptive granulated inert material or by applying active compound concentrates by means of adhesives, for example polyvinyl alcohol, sodium polyacrylate or, alternatively, mineral oils, to the surface of support substances such as sand or kaolinites or of granulated inert material. Suitable active compounds can also be granulated in the customary manner for the preparation of fertilizer granules - if desired mixed with fertilizers.

In wettable powders the active compound concentration is, for example, about 10 to 90% by weight, the remainder to 100% by weight is composed of customary formulation components. In the case of emulsifiable concentrates, the active compound concentration can be about 5 to 80% by weight. Dust-like formulations contain mostly 5 to 20% by weight of active compound, sprayable solutions about 2 to 20% by weight of active compound. In the case of granules, the active compound content partially depends on whether the active compound is liquid or solid and which granulation auxiliaries, fillers etc. are used.

In addition, said active compound formulations optionally contain the adhesives, wetting agents, dispersants, emulsifiers, penetrants, solvents, fillers or support substances customary in each case.

For application, the concentrates present in commercial form are optionally diluted in a customary manner, for example by means of water in the case of wettable powders, emulsifiable concentrates, dispersions and sometimes even in the case of microgranulates. Dust-like and granulated preparations, and sprayable solutions are customarily not diluted further with other inert substances before application.

The application rate required varies with the external conditions such as temperature, humidity and the like. It can vary within wide limits, for example between 0.005 and 10.0 kg/ha or more of active substance, but it is preferably between 0.01 and 5 kg/ha.

The active compounds according to the invention in their commercial formulations can be applied either alone or in combination with other fungicides known from the literature.

Examples of fungicides known from the literature which, according to the invention, can be combined with the compounds of the formula I are the following products:
imazalil, prochloraz, fenapanil, SSF 105, triflumizol, PP 969, flutriafol, BAY-MEB 6401, propiconazole, etaconazole, diclobutrazol, bitertanol, triadimefon, triadimenol, fluotrimazole, tridemorph, dodemorph, fenpropimorph, falimorph, S-32165, chlobenzthiazone, parinol, buthiobate, fenpropidin, triforine, fenarimol, nuarimol, triarimol, ethirimol, dimethirimol, bupirimate, rabenzazole, tricyclazole, fluobenzimine, pyroxyfur, NK-483, PP-389, pyroquilon, hymexazole, fenitropan, UHF-8227, cymoxanil, dichlorunanid [sic], captafol, captan, folpet, tolylfluanid, chlorothalonil, etridiazole, iprodione (formula II), procymidone, vinclozolin, metomeclan, myclozolin, dichlozolinate, fluorimide, drazoxolan, quinomethionate, nitrothal-isopropyl, dithianon, dinocap, binapacryl,
fentin acetate, fentin hydroxide, carboxin, oxycarboxin, pyracarbolid, methfuroxam, fenfura [sic], furmecyclox, benodanil, mebenil, mepronil, flutalanil, fuberidazole, thiabendazole, carbendazim, benomyl, thiofante [sic], thiofanate-methyl [sic], CGD-94340 F, IKF-1216,
mancozeb, maneb, zineb, nabam, thiram, probineb, prothiocarb, propamocarb, dodine, guazatine, dicloran, quintozene, chloroneb, tecnazene, biphenyl, anilazine, 2-phenylphenol, copper compounds such as Cu oxychloride, oxine Cu, Cu oxides, sulfur, fosetylaluminum [sic],

sodium dodecylbenzenesulfonate,
sodium dodecyl sulfate,
sodium C13/C15 alcohol ether sulfonate,
sodium cetostearylphosphate ester,
dioctyl sodium sulfosuccinate,
sodium isopropylnaphthalenesulfonate,
sodium methylenebisnaphthalenesulfonate,
cetyltrimethylammonium chloride,

Salts of long-chain primary, secondary or tertiary amines, alkylpropylenamines, laurylpyridinium bromide, ethoxylated quaternized fatty amines, alkyldimethylbenzylammonium chloride and 1-hydroxyethyl-2-alkylimidazoline.

The abovementioned combination components are known active compounds, many of which are described in CH [sic].R. Worthing, U. [sic] S.B. Walker, "The Pesticide Manual", 7th Edition (1983), British Crop Protection Council.

The active compounds according to the invention, in particular those of the examples mentioned, can in addition be present in their commercial formulations and in the application forms prepared from these formulations mixed with other active compounds, such as insecticides, attractants, sterilants, acaricides, nematicides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphoric acid esters, carbamates, carboxylic acid esters, formamidines, tin compounds, substances produced by microorganisms and the like. Preferred mixture components are:

1. from the phosphoric acid ester group azinphos-ethyl, azinphos-methyl, 1-(4-chlorophenyl)-4-(O-ethyl, S-propyl)phosphoryl-oxypyrazole (TIA-230), chlorpyrifos, coumaphos, demeton, demeton-S-methyl, diazinon, dichlorvos, dimethoate, ethoprophos, etrimfos, fenitrothion, fenthion,

heptenophos, parathion, parathion-methyl, phosalone, pirimiphos-ethyl, pirimiphos-methyl, profenofos, prothiofos, sulprofos, triazophos or trichlorophon.

2. from the carbamate group
aldicarb, bendiocarb, BPMC (2-(1-methylpropyl)-phenylmethyl carbamate), butocarboxim, butoxycarboxim, carbaryl, carbofuran, carbosulfan, cloethocarb, isoprocarb, methomyl, oxamyl, primicarb [sic], promecarb, propoxur or thiodicarb.

3. from the carboxylic acid ester group
allethrin, alphamethrin, bioallethrin, bioresmethrin, cycloprothrin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, alpha-cyano-3-phenyl-2-methylbenzyl 2,2-dimethyl-3-(2-chloro-2-trifluoromethylvinyl)-cyclopropanecarboxylate (FMC 54800), fenpropathrin, fenfluthrin, fenvalerate, flucythrinate, flumethrin, fluvalinate, permethrin, resmethrin or tralomethrin.

4. from the formamidine group
amitraz or chlordimeform

5. from the tin compound group
azocyclotin, cyhexatin and fenbutatin oxide

6. Miscellaneous
abamektin, Bacillus thuringiensis, bensultap, binapacryl, bromopropylate, buprofecin, camphechlor, cartap, chlorobenzialate [sic], chlorfluazuron, 2-(4-chlorophenyl)-4,5-diphenylthiophene (UBI-T 930), chlofentezine, 2-naphthylmethyl cyclopropanecarboxylate (Ro 12-0470), cyromacin, DDT, dicofol, N-(3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenylamino)carbonyl)-2,6-difluorobenzamide (XRD 473), diflubenzuron, N-(2,3-dihydro-3-methyl-1,2-thiazol-2-ylidene)-2,4-xylidine, dinobuton, dinocap, endosulfan, fenoxycarb, fenthiocarb [sic],

flubenzimine, flufenoxuron, gamma-HCH, hexythiazox, hydramethylnon (AC 217 300), ivermectin, 2-nitromethyl-4,5-dihydro-6H-thiazine (SD 52618), 2-nitromethyl-3,4-dihydrothiazole (SD 35651), 2-nitromethylene-1,3-thiazinan-3-yl-carbamaldehyde [sic] (WL 108 477), propargite, teflubenzuron, tetradifon, tetrasul, thiocyclam, triflumaron, core polyhedrosis and granulosis viruses.

The active compound content of the application forms prepared from the commercial formulations can vary within wide ranges, and the active compound concentration of the application forms can be from 0.0001 up to 100% by weight of active compound, preferably between 0.001 and 1% by weight. Application is carried out in one of the customary ways suited to the application forms.

The following examples serve to illustrate the invention.

A. **Formulation examples**

a) A dusting agent is obtained by mixing 10 parts by weight of active compound and 90 parts by weight of talc as the inert substance and comminuting the mixture in a hammer mill.

b) A wettable powder which is easily dispersible in water is obtained by mixing 25 parts by weight of active compound, 65 parts by weight of kaolin-containing quartz as the inert substance, 10 parts by weight of potassium ligninsulfonate and 1 part by weight of sodium oleoylmethyltaurate as the wetting agent and dispersant and grinding the mixture in a pinned disk mill.

c) A dispersion concentrate which is easily dispersible in water is obtained by mixing 40 parts by weight of active compound with 7 parts by weight of a sulfosuccinic acid half-ester, 2 parts by weight of a

sodium ligninsulfonate and 51 parts by weight of water and grinding the mixture in a friction ball mill to a fineness of less than 5 microns.

d) An emulsifiable concentrate can be prepared from 15 parts by weight of active compound, 75 parts by weight of cyclohexanone as the solvent and 10 parts by weight of oxyethylated nonylphenol (10 EO) as the emulsifier.

e) Granules can be prepared from 2 to 15 parts by weight of active compound and an inert granulate support material such as attapulgite, pumice granules and/or quartz sand. Expediently, a suspension of the wettable powder from Example b) having a solids content of 30% is used and this is sprayed onto the surface of attapulgite granules, dried and mixed intimately. The weight content of the wettable powder here is about 5% and that of the inert support material is about 95% of the finished granules.

B. Chemical examples

4-Benzyl-2-(6-methylpyridin-2-yl)pyrimidine (Example No.:1)

0.2 g of 5% palladium/carbon is added to a solution of 1.48 g (0.005 mol) of 4-benzyl-2-(6-methylpyridin-2-yl)-6-chloropyrimidine in 50 ml of ethanol. This mixture is brought into contact with hydrogen under a pressure of 3 bar and at a temperature of 60°C with vigorous stirring for 2 h. The catalyst is then filtered off and the filtrate is concentrated in vacuo. The residue is taken up in water, and the solution is saturated with sodium bicarbonate and extracted with CH_2Cl_2. The organic phase is dried over Na_2SO_4 and concentrated. 1.25 g (95.7%) of a colorless oil are obtained.

4-Benzyl-2-(6-methylpyridin-2-yl)-6-methoxypyrimidine (Example No.: 2)

A sodium methylate solution is prepared by dissolving 0.184 g (0.008 mol) of sodium in 40 ml of abs. methanol. 1.30 g (0.0044 mol) of 4-benzyl-2-(6-methylpyridin-2-yl)-6-chloropyrimidine are added to this solution and the mixture is boiled under reflux for 3 h. It is then concentrated, water is added to the residue and the mixture is extracted with methylene chloride. The organic phase is dried using Na_2SO_4 and concentrated. 1.16 g (90.5%) of a yellowish oil are obtained.

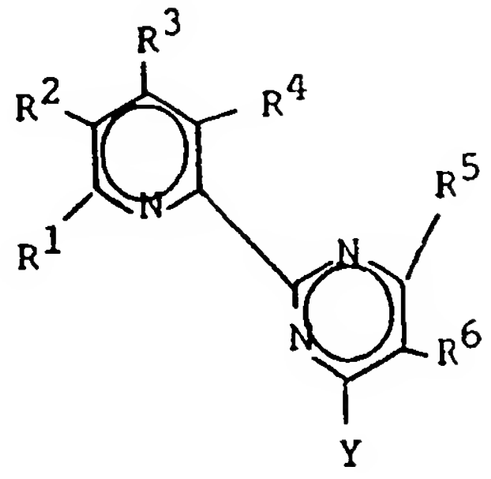
4-Benzyl-2-(6-methylpyridin-2-yl)-6-methylmercapto-pyrimidine (Example No.: 3)

0.45 g (0.0065 mol) of sodium thiomethylate are added to a solution of 1.3 g (0.0044 mol) of 4-benzyl-2-(6-methyl-pyridin-2-yl)-6-chloropyrimidine in 50 ml of abs. acetonitrile and the mixture is allowed to boil under reflux for 4 h. The solid is filtered off and the filtrate is concentrated. The residue is taken up in water and the solution is extracted with methylene chloride. The extract is dried over Na_2SO_4 and concentrated in vacuo, and 1.13 g (83.5%) of a yellowish oil are obtained.

The compounds of Table A can be prepared analogously to these examples.

Abbreviations: Me = methyl
Et = ethyl
Pr = propyl
Bu = butyl

Table A



(I)

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
1.1	CH_3	H	H	H	H	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,81 d8,18 t7,82 m7,42-7,21 s4,20 s2,60
1.2	CH_3	H	H	H	OCH_3	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,24 t7,70 m7,34-7,26 s6,33 s4,23 s4,04 s2,71
1.3	CH_3	H	H	H	SCH_3	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,28 t7,71 m7,38-7,19 s6,76 s4,22 s2,73 s2,60
1.4	CH_3	H	H	H	$OCH_2C{\equiv}CH$	H	CH_2-C_6H_5	
1.5	CH_3	H	H	H	CH_3	H	CH_2-C_6H_5	

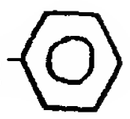
Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
1.6	CH_3	H	H	H	C_2H_5	H	$CH_2-C_6H_5$	
1.7	CH_3	H	H	H	C_6H_5	H	$CH_2-C_6H_5$	
1.8	CH_3	H	H	H	$CH_2C_6H_5$	H	$CH_2-C_6H_5$	
1.9	CH_3	H	H	H	C_3H_7	H	$CH_2-C_6H_5$	
1.10	CH_3	H	H	H	OC_2H_5	H	$CH_2-C_6H_5$	
1.11	CH_3	H	H	H	OC_4H_9	H	$CH_2-C_6H_5$	
1.12	CH_3	H	H	H	$SCH_2C_6H_5$	H	$CH_2-C_6H_5$	
1.13	CH_3	H	H	H	$OCH_2C_6H_5$	H	$CH_2-C_6H_5$	
1.14	CH_3	H	H	H	SC_2H_5	H	$CH_2-C_6H_5$	
1.15	CH_3	H	H	H	CH_2CH_2- 	H	$CH_2-C_6H_5$	
1.16	CH_3	H	H	H	H	Br	$CH_2-C_6H_5$	

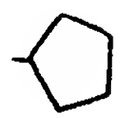
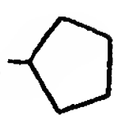
Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
1.17	CH_3	H	H	H	H	Cl	CH_2-C_6H_5	
1.18	CH_3	H	H	H	OCH_3	Cl	CH_2-C_6H_5	
1.19	CH_3	H	H	H	C_2H_5	Br	CH_2-C_6H_5	
1.20	CH_3	H	H	H	H	H	CH_2-4-Cl-C_6H_4	
1.21	CH_3	H	H	H	OCH_3	H	CH_2-4-Cl-C_6H_4	
1.22	CH_3	H	H	H	C_2H_5	H	CH_2-4-Cl-C_6H_4	
1.23	CH_3	H	H	H	OEu	H	CH_2-4-Cl-C_6H_4	
1.24	CH_3	H	H	H	SMe	H	CH_2-4-Cl-C_6H_4	
1.25	CH_3	H	H	H	Me	H	CH_2-4-Cl-C_6H_4	
1.26	CH_3	H	H	H	Et	H	CH_2-4-Cl-C_6H_4	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
1.27	CH_3	H	H	H	CH_2-C_6H_5	H	CH_2-4-Cl-C_6H_4	
1.28	CH_3	H	H	H	H	Cl	CH_2-4-Cl-C_6H_4	
1.29	CH_3	H	H	H	OC_4H_9	H	CH_2-2-Cl-C_6H_4	
1.30	CH_3	H	H	H	SCH_2- 	H	CH_2-2-Cl-C_6H_4	
1.31	CH_3	H	H	H	Me	H	CH_2-3-Cl-C_6H_4	
1.32	CH_3	H	H	H	Et	Br	CH_2-3-Cl-C_6H_4	
1.33	CH_3	H	H	H	O-4-Cl-C_6H_4	H	CH_2-4-Br-C_6H_4	
1.34	CH_3	H	H	H	S-4-Br-C_6H_4	H	CH_2-4-CF_3-C_6H_4	
2.1	CH_3	CH_3	H	H	H	H	CH_2-C_6H_5	
2.2	CH_3	CH_3	H	H	Et	H	CH_2-C_6H_5	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
2.3	CH_3	CH_3	H	H		Br	CH_2-C_6H_5	
2.4	CH_3	CH_3	H	H		Cl	CH_2-C_6H_5	
2.5	CH_3	CH_3	H	H	CH_2CH_2- 	H	CH_2-C_6H_5	
2.6	CH_3	CH_3	H	H	$SCH_2C_6H_5$	C_2H_5	CH_2-C_6H_5	
2.7	CH_3	CH_3	H	H	$OCH_2C_6H_5$	C_4H_9	CH_2-4-CH_3-C_6H_4	
2.8	CH_3	CH_3	H	H	OCH_2-$CH=CH_2$	$CH(CH_3)_2$	CH_2-3-CH_3-C_6H_4	
2.9	CH_3	CH_3	H	H	OCH_3	H	$CH_2C_6H_5$	m.p. : 100 °C
2.10	CH_3	CH_3	H	H	H	H	$CH_2C_6H_5$	m.p. : 115 °C
2.11	CH_3	CH_3	H	H	H	H	CH_3-4-Cl-C_6H_4	
2.12	CH_3	CH_3	H	H	OCH_3	H	CH_2-4-Cl-C_6H_4	
2.13	CH_3	CH_3	H	H	SCH_3	H	CH_2-4-Cl-C_6H_4	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
2.14	CH_3	CH_3	H	H	H	H	CH_2-4-F-C_6H_4	
2.15	CH_3	CH_3	H	H	H	Cl	CH_2-4-F-C_6H_4	
2.16	CH_3	CH_3	H	H	OCH_3	H	CH_2-4-F-C_6H_4	
2.17	CH_3	CH_3	H	H	SCH_3	H	CH_2-4-F-C_6H_4	
2.18	CH_3	CH_3	H	H	H	H	CH_2-2,4-Cl_2-C_6H_3	
2.19	CH_3	CH_3	H	H	H	Br	CH_2-2,4-Cl_2-C_6H_3	
2.20	CH_3	CH_3	H	H	OC_2H_5	H	CH_2-2,4-Cl_2-C_6H_3	
2.21	CH_3	CH_3	H	H	S-CH_2-C≡CH	H	CH_2-2,4-Cl_2-C_6H_3	
2.22	CH_3	CH_3	H	H	SCH_3	H	CH_2-2,4-Cl_2-C_6H_3	
2.23	CH_3	CH_3	H	H	H	H	CH_2-4-OCH_3-C_6H_4	
2.24	CH_3	CH_3	H	H	OCH_3	H	CH_2-4-OCH_3-C_6H_4	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
2.25	CH_3	CH_3	H	H	OCH_2-CH=CH_2	H	CH_2-4-OCH_3-C_6H_4	
3.1	CH_3	H	CH_3	H	H	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,67 s8,06 s7,01 d6,90 s4,16 s2,60 s2,32
3.2	CH_3	H	CH_3	H	Me	H	CH_2-C_6H_5	
3.3	CH_3	H	CH_3	H	OCH_3	H	CH_2-4-OCH_3-C_6H_4	
3.4	CH_3	H	CH_3	H	SCH_3	H	CH_2-3-CF_3-C_6H_4	
3.5	CH_3	H	CH_3	H	OCH_2-C_6H_5	H	CH_2-4-CN-C_6H_4	
3.6	CH_3	H	CH_3	H	OC_6H_5	H	CH_2-C_6H_5	
3.7	CH_3	H	CH_3	H	S-4-Cl-C_6H_4	H	CH_2-C_6H_5	
3.8	CH_3	H	CH_3	H	C_3H_7	H	CH_2-4-Cl-C_6H_4	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
3.9	CH_3	H	CH_3	H	$CH_2C_6H_5$	H	CH_2-C_6H_5	
3.10	CH_3	H	CH_3	H	$CH_2CH_2C_6H_5$	H	CH_2-C_6H_5	
3.11	CH_3	H	CH_3	H	H	C_2H_5	CH_2-C_6H_5	
3.12	CH_3	H	CH_3	H	Et	C_2H_5	CH_2-C_6H_5	
3.13	CH_3	H	CH_3	H	Me	CH_3	CH_2-C_6H_5	
3.14	CH_3	H	CH_3	H	H	CH_3	CH_2-C_6H_5	
3.15	CH_3	H	CH_3	H	H	C_3H_7	CH_2-C_6H_5	
3.16	CH_3	H	CH_3	H	OCH_3	H	$CH_2C_6H_5$	^{1}H-NMR ($CDCl_3$): s8.06 s7.09 s6.30 s4.24 s4.05 s2.67 s2.39

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
3.17	CH_3	H	CH_3	H	SCH_3	H	$CH_2C_6H_5$	^{1}H-NMR ($CDCl_3$): s8,10 s7,12 s6,76 s4,22 s2,65 s2,59 s2,39
4.1	H	H	C_2H_5	H	H	H	CH_2-C_6H_5	
4.2	H	H	C_2H_5	H	OCH_3	Br	CH_2-4-$OCHF_2$-C_6H_4	
4.3	H	H	C_2H_5	H	$OCH_2CH=CH_2$	H	CH_2-4-Cl-C_6H_4	
4.4	H	H	C_2H_5	H	OCH_2-C≡CH	H	CH_2-C_6H_5	
4.5	H	H	C_2H_5	H	OCH_2-CH=CH-CH_3	C_4H_9	CH_2-C_6H_5	
4.6	H	H	C_2H_5	H	CH_3	Cl	CH_2-C_6H_5	
4.7	H	H	C_2H_5	H	$CH_2C_6H_5$	Br	CH_2-C_6H_5	
4.8	H	H	C_2H_5	H	SC_3H_7	H	CH_2-C_6H_5	

2068328

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
5.1	H	H	C_6H_5	H	H	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,87 s(br)8,78 d7,02 s4,29
5.2	H	H	C_6H_5	H	H	H	CH_2-4-Cl-C_6H_4	
5.3	H	H	C_6H_5	H	H	Br	CH_2-C_6H_5	
5.4	H	H	C_6H_5	H	OCH_3	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,89 s(br)8,72 s6,39 s4,25 s4,06
5.5	H	H	C_6H_5	H	OC_2H_5	H	CH_2-C_6H_5	
5.6	H	H	C_6H_5	H	SCH_3	H	CH_2-3-Cl-C_6H_4	
5.7	H	H	C_6H_5	H	$SCH_2C_6H_5$	H	$CH_2C_6H_5$	^{1}H-NMR ($CDCl_3$): d8,89 s(br)8,69 s6,81 s4,49 s4,24

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
5.8	H	H	C_6H_5	H	SCH_3	H	$CH_2C_6H_5$	^{1}H-NMR ($CDCl_3$): d8,89 s(br)8,76 s6,83 s4,24 s2,63
6.1	C_3H_7	H	H	H	H	H	CH_2-C_6H_5	
6.2	C_3H_7	H	H	H	OEt	H	CH_2-C_6H_5	
6.3	C_3H_7	H	H	H	OCH_3	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,21 t7,71 s6,35 s4,21 s4,03 t2,94 tq1,85 t1,02
6.4	C_3H_7	H	H	H	$OCH_2CH=CH_2$	H	CH_2-C_6H_5	
6.5	C_3H_7	H	H	H	SCH_3	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8,25 t7,74 s6,80 s4,20 t2,93 s2,60 tq1,84 t1,02
6.6	C_3H_7	H	H	H	OC_4H_9	H	CH_2-C_6H_5	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
6.7	C_3H_7	H	H	H	$SCH_2C_6H_5$	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8.22 t7.71 s6.74 s4.50 s4.15 t2.96 tq1.85 t1.01
6.8	C_3H_7	H	H	H	H	Br	CH_2-C_6H_5	
6.9	C_3H_7	H	H	H	H	H	CH_2-4-Cl-C_6H_4	
6.10	C_3H_7	H	H	H	H	H	CH_2-2-Cl-C_6H_4	
6.11	C_3H_7	H	H	H	C_6H_5	H	CH_2-4-Cl-C_6H_4	
6.12	C_3H_7	H	H	H	$OCH_2C_6H_5$	H	CH_2-C_6H_5	
6.13	C_3H_7	H	H	H	OCH_2-4-Cl-C_6H_4	H	CH_2-C_6H_5	
6.14	C_3H_7	H	H	H	SCH_2-4-Cl-C_6H_4	H	CH_2-C_6H_5	
6.15	C_3H_7	H	H	H	OC_2H_4-OC_2H_5	H	CH_2-C_6H_5	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
6.16	C_3H_7	H	H	H	SC_2H_4-SC_2H_5	H	CH_2-C_6H_5	
6.17	C_3H_7	H	H	H	OC_4H_9	Cl	CH_2-C_6H_5	
6.18	C_3H_7	H	H	H	Cl	H	$CH_2C_6H_5$	m.p.: 82 °C
6.19	C_3H_7	H	H	H	OCH_3	H	CH_2-4-Cl-C_6H_4	
6.20	C_3H_7	H	H	H	SCH_3	H	CH_2-4-Cl-C_6H_4	
6.21	C_3H_7	H	H	H	CH_3	H	CH_2-4-Cl-C_6H_4	
6.22	C_3H_7	H	H	H	H	H	CH_2-4-F-C_6H_4	
6.23	C_3H_7	H	H	H	OC_2H_5	H	CH_2-4-F-C_6H_4	
6.24	C_3H_7	H	H	H	OCH_3	H	CH_2-4-F-C_6H_4	
6.25	C_3H_7	H	H	H	H	H	CH_2-2,4-Cl_2-C_6H_3	
6.26	C_3H_7	H	H	H	OCH_3	H	CH_2-2,4-Cl_2-C_6H_3	
6.27	C_3H_7	H	H	H	H	H	CH_2-4-OCH_3-C_6H_4	

2063328

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
6.28	C_3H_7	H	H	H	SCH_3	H	CH_2-4-OCH_3-C_6H_4	
7.1	$CH_2C_6H_5$	H	H	H	OCH_3	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8.26 t7.69 m7.39-7.19 d7.09 s6.36 s4.39 s4.24 s4.06
7.2	$CH_2C_6H_5$	H	H	H	SCH_3	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8.28 t7.69 m7.38-7.20 s6.82 s4.36 s4.20 s2.61
7.3	$CH_2C_6H_5$	H	H	H	$SCH_2C_6H_5$	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8.25 t7.69 m7.69-7.18 d7.12 s6.79 s4.51 s4.38 s4.18
7.4	$CH_2C_6H_5$	H	H	H	H	H	CH_2-C_6H_5	^{1}H-NMR ($CDCl_3$): d8.79 d8.34 t7.70 m7.37-7.21 d7.15 d7.02 s4.41 s4.24
7.5	$CH_2C_6H_5$	H	H	H	C_2H_5	H	CH_2-C_6H_5	
7.6	$CH_2C_6H_5$	H	H	H	H	Cl	CH_2-C_6H_5	
7.7	$CH_2C_6H_5$	H	H	H	H	Br	CH_2-C_6H_5	

2068328

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
7.8	$CH_2C_6H_5$	H	H	H	OC_4H_9	H	CH_2-C_6H_5	
7.9	$CH_2C_6H_5$	H	H	H	CH_3	H	CH_2-C_6H_5	
8.1	$(CH_3)_2CH$	H	H	H	H	H	CH_2CH_2-C_6H_5	
8.2	$(CH_3)_2CH$	H	H	H	CH_3	Br	CH_2CH_2-4-Cl-C_6H_4	
8.3	$(CH_3)_2CH$	H	H	H	OCH_3	H	CH_2CH_2-C_6H_5	
8.4	$(CH_3)_2CH$	H	H	H	SCH_2-4-Cl-C_6H_4	H	CH_2CH_2-C_6H_5	
8.5	C_4H_9	H	H	H	OCH_2-CH=CH_2	H	$CHCH_3CH_2C_6H_5$	
8.6	CH_3	CH_3	H	H	SCH_2-CH=CH_2	Cl	$CHCH_3CH_2C_6H_5$	
8.7	CH_3	CH_3	H	H	$OCH_2CH_2OCH_2CH_3$	H	$CHC_2H_5CH_2C_6H_5$	
8.8	H	H	C_2H_5	H	C_6H_5	H	$CH_2CHCH_3C_6H_5$	
8.9	H	H	C_2H_5	H	4-Cl-C_6H_4	H	$CH_2CHCH_3C_6H_5$	

Continuation of Table A

No.	R^1	R^2	R^3	R^4	R^5	R^6	Y	Physical characteristics
8.10	C_2H_5	H	H	H	H	H	$CH_2C_6H_5$	
8.11	C_2H_5	H	H	H	H	H	CH_2-4-Cl-C_6H_4	
8.12	C_2H_5	H	H	H	H	H	CH_2-4-F-C_6H_4	
8.13	C_2H_5	H	H	H	H	H	CH_2-2,4-Cl_2-C_6H_3	
8.14	C_2H_5	H	H	H	H	H	CH_2-4-OCH_3-C_6H_4	

C. Biological Examples

Example 1

Rice plants of the "Ballila" type about 5 weeks old were treated with the concentration of the claimed compounds indicated below after prespraying with 0.05% strength gelatine solution. After the spray coating had dried on, the plants were uniformly inoculated with a spore suspension of Piricularia oryzae and placed for 48 h in a climatic chamber, which was kept dark, having a temperature of 25°C and 100% relative atmospheric humidity. The rice plants were then cultivated further in a greenhouse having a temperature of 25°C and 80% relative atmospheric humidity. Evaluation of attack was carried out after 5 days. The degree of attack was expressed in % of attacked leaf surface in comparison to untreated infected control plants. The results are collated in Table 1.

Table 1

Compound according to Example	Leaf surface attacked with Piricularia oryzae in % at mg of active compound/liter of spray liquor 500
1.4	0
1.1	0
1.2	0
1.3	0
2.9	0
2.10	0
3.1	0
6.5	0
6.3	0
untreated infected plants	100

Example 2

Barley plants were heavily inoculated in the 2-leaf stage with barley mildew conidia (Erysiphe graminis hordei) and cultivated further in a greenhouse at 20°C and a relative atmospheric humidity of about 50%. 1 day after inoculation, the plants were wetted uniformly with the compounds listed in Table 2 at the active compound concentration indicated. After an incubation time of 7-9 days, the plants were examined for attack by barley mildew. The degree of attack is expressed in % of attacked leaf surface, relative to untreated infected control plants (= 100% attack). The result is summarized in Table 2.

Table 2

Compound according to Example	Leaf surface attacked with barley mildew in % at mg of active compound/liter of spray liquor 500
1.1	0
1.2	0
1.3	0
2.9	0
6.3	0
untreated infected plants	100

Example 3

Broad beans of the "Herz Freya" or "Frank's Ackerperle" type about 14 days old were treated with aqueous suspensions of the claimed compounds until dripping wet.

After the spray coating had dried on, the plants were inoculated with a spore suspension (1.5 million

spores/ml) of Botrytis cinerea. The plants were cultivated further in a climatic chamber at 20-22°C and about 99% relative atmospheric humidity. The infection of the plants is manifested by the formation of black spots on the leaves and stalks. Evaluation of the tests was carried out 1 week after inoculation.

The degree of action of the test substances was assessed as a percentage of the untreated infected control and is reproduced in Table 3.

Table 3

Compound according to Example	Leaf surfaces attacked with Botrytis cinerea in % at mg of active compound/liter of spray liquor
	500
1.2	0
1.3	0
2.9	0
2.10	0
3.16	0
6.3	0
6.7	0
untreated infected plants	100

Example 4

Wheat plants of the "Jubilar" type were treated in the 2-leaf stage with aqueous suspensions of the preparations given in Table 4 until dripping wet.

After the spray coating had dried on, the plants were inoculated with an aqueous pyknospore suspension of Leptosphaeria nodorum and incubated at 100% relative atmospheric humidity in a climatic chamber for several

hours. Until expression of symptoms, the plants were further cultivated in a greenhouse at about 90% relative atmospheric humidity.

The degree of action is expressed as a percentage of the untreated infected control and is reproduced in Table 4.

Table 4

Compound according to Example	Leaf surfaces attacked with Leptosphaeria nodorum in % at mg of active compound/ liter of spray liquor
	500
1.4	0
1.1	0
1.2	0
1.3	0
7.1	0
7.2	0
7.4	0
5.1	0
2.9	0
2.10	0
3.16	0
3.17	0
3.1	0
6.18	0
6.5	0
6.3	0
untreated infected plants	100

Example 5

Wheat of the "Jubilar" type was treated in the 2-leaf stage with aqueous suspensions of the claimed compounds until dripping wet. After the spray coating had dried on, the plants were inoculated with an aqueous spore

suspension of Puccinia recondita. The plants were placed dripping wet in a climatic chamber at 20°C and about 100% relative atmospheric humidity for about 16 hours. The infected plants were then cultivated further in a greenhouse at a temperature of 22-25°C and 50-70% relative atmospheric humidity.

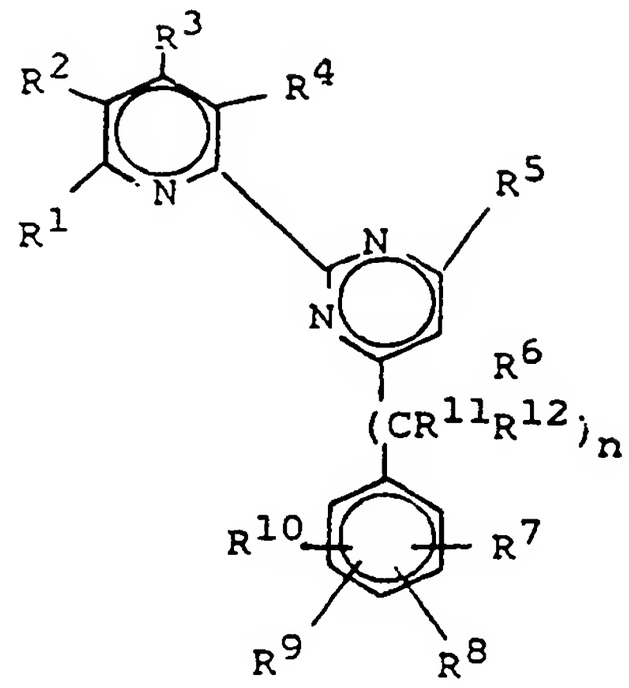
After an incubation time of about 2 weeks, the fungi sporulates onto the entire leaf surface of the untreated control plants such that an evaluation of attack of the test plants can be carried out. The degree of attack was expressed in % of attacked leaf surface in comparison to untreated infected control plants and is reproduced in Table 5.

Table 5

Compound according to Example	Leaf surface attacked with Puccinia recondita in % at mg of active compound/liter of spray liquor
	500
1.1	0
1.2	0
6.3	0
1.3	0
untreated infected plants	100

Patent claims:

1. A compound of the formula I



(I)

in which

R^1 is hydrogen, (C_1-C_6)alkyl, (C_1-C_4)alkoxy-(C_1-C_4)-alkyl, (C_1-C_4)alkylthio-(C_1-C_4)alkyl, (C_2-C_6)alkenyl, (C_2-C_6)alkynyl, (C_3-C_7)cycloalkyl, (C_3-C_7)-cycloalkyl(C_1-C_4)alkyl, it being possible for the two last-mentioned radicals to be monosubstituted to trisubstituted in the cycloalkyl moiety by (C_1-C_4)alkyl, or phenyl, phenoxy-(C_1-C_4)alkyl, phenylmercapto(C_1-C_4)alkyl, phenyl-(C_1-C_4)alkyl or phenoxy-phenoxy(C_1-C_4)alkyl, it being possible for the five last-mentioned radicals to be monosubstituted to trisubstituted in the phenyl moiety by halogen, nitro, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl or (C_1-C_4)haloalkoxy,

R^2, R^3 and R^4 are independently of one another hydrogen, (C_1-C_6)alkyl or phenyl, it being possible for the phenyl radical to be monosubstituted to trisubstituted by halogen, nitro, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl, or (C_1-C_4)haloalkoxy,

R^5 is hydrogen, (C_1-C_6)alkyl, (C_3-C_7)cycloalkyl, (C_3-C_7)cycloalkyl-(C_1-C_4)alkyl, it being possible for the two last-mentioned radicals to be

monosubstituted to trisubstituted in the cycloalkyl moiety by (C_1-C_4)alkyl, (C_1-C_4)haloalkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)alkoxy-(C_1-C_4)alkyl, (C_1-C_4)alkylthio-(C_1-C_4)alkyl, halogen, (C_2-C_6)alkenyl, (C_2-C_6)alkynyl, phenyl, phenoxy, phenyl(C_1-C_4)alkyl, phenoxy-(C_1-C_4)alkyl, phenylmercapto-(C_1-C_4)alkyl, phenylmercapto, phenyl-(C_1-C_4)alkoxy or phenyl-(C_1-C_4)alkylthio, it being possible for the eight last-mentioned radicals to be monosubstituted to trisubstituted in the phenyl moiety by halogen, nitro, cyano, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl or (C_1-C_4)haloalkoxy, or (C_2-C_4)alkenyloxy, (C_2-C_4)alkynyloxy, (C_1-C_4)haloalkoxy, (C_1-C_4)alkoxy-(C_1-C_4)alkoxy or (C_1-C_4)alkylthio-(C_1-C_4)alkylthio,

R^6 is hydrogen, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_2-C_6)-alkenyloxy, (C_2-C_6)alkynyloxy, (C_1-C_4)alkylthio, halogen or phenyl, it being possible for the phenyl radical to be monosubstituted to trisubstituted by halogen, nitro, cyano, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl or (C_1-C_4)haloalkoxy,

R^7, R^8, R^9 and R^{10} are independently of one another hydrogen, halogen, nitro, cyano, (C_1-C_4)alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)haloalkyl or (C_1-C_4)haloalkoxy,

R^{11} and R^{12} are independently of one another hydrogen or (C_1-C_4)alkyl and

n is 1-3, and their acid addition salts.

2. A compound of the formula I of claim 1, in which

R^1 is hydrogen, (C_1-C_8)alkyl, phenyl, phenyl-(C_1-C_2)-alkyl, phenoxy-phenoxy-(C_1-C_2)alkyl or phenoxy-(C_1-C_2)alkyl, it being possible for the four last-mentioned radicals to be monosubstituted to trisubstituted in the phenyl moiety by halogen or (C_1-C_4)alkyl; or (C_1-C_3)alkoxy-(C_1-C_2)alkyl,

R^2 and R^3 are independently of one another hydrogen, (C_1-C_3)alkyl or phenyl, it being possible for the phenyl radical to be monosubstituted to trisubstituted by halogen or (C_1-C_4)alkyl,

R^4 is hydrogen,

R^5 is hydrogen, (C_1-C_6)alkyl, (C_3-C_6)cycloalkyl, (C_5-C_6)cycloalkyl-(C_1-C_3)alkyl, phenyl, phenyl-(C_1-C_2)alkylthio, phenyl-(C_1-C_2)alkyl, it being possible for the three last-mentioned radicals to be monosubstituted to trisubstituted in the phenyl moiety by halogen, (C_1-C_4)alkyl, (C_1-C_3)-haloalkyl or (C_1-C_4)alkoxy, or (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_2-C_4)alkenyloxy, (C_2-C_4)alkynyl-oxy, (C_2-C_3)alkenyl, (C_2-C_4)alkynyl or (C_1-C_4)alk-oxy-(C_1-C_4)alkoxy,

R^6 is hydrogen, (C_1-C_4)alkyl, halogen, phenyl or (C_1-C_3)alkoxy,

R^7, R^8, R^9 and R^{10} are independently of one another hydrogen, (C_1-C_4)alkyl, (C_1-C_4)haloalkyl or (C_1-C_4)-alkylthio,

R^{11} and R^{12} are hydrogen,

and n = 1, and their acid addition salts.

3. A process for the preparation of compounds of the formula I as claimed in claim 1 or 2, which comprises

a) for compounds where R^5 = hydrogen, reductively dehalogenating an appropriate halopyrimidine of the formula I where R^5 = halogen and all other substituents have the meanings mentioned, or

b) for compounds of the formula I in which R^5 is (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, phenoxy, phenyl-mercapto, phenyl-(C_1-C_4)alkoxy or phenyl-(C_1-C_4)alkyl-thio, it being possible for the 4 last-mentioned radicals in the phenyl moiety to be monosubstituted to trisubstituted by halogen, nitro, cyano, (C_1-C_4)-alkyl, (C_1-C_4)alkoxy, (C_1-C_4)alkylthio, (C_1-C_4)halo-alkyl or (C_1-C_4)haloalkoxy, or (C_2-C_4)alkenyloxy, (C_2-C_4)alkynyloxy, (C_1-C_4)haloalkoxy, (C_1-C_4)alkoxy-

(C_1-C_4)alkoxy or (C_1-C_4)alkylthio-(C_1-C_4)alkylthio, reacting an appropriate halopyrimidine of the formula I where R^5 = halogen with an alkali metal compound of the formula II

$$R^5\text{-}Y \qquad (II),$$

in which R^5 has the abovementioned meaning and Y is an alkali metal, or

c) for compounds of the formula I in which R^5 is (C_1-C_6)alkyl, (C_3-C_7)cycloalkyl, (C_3-C_7)cycloalkyl-(C_1-C_4)alkyl, (C_1-C_4)alkoxy-(C_1-C_4)alkyl, (C_1-C_4)alkylthio-(C_1-C_4)alkyl or phenyl, it being possible for the last-mentioned radical to be monosubstituted to trisubstituted by (C_1-C_4)alkyl or (C_1-C_4)alkoxy, reacting an appropriate halopyrimidine of the formula I where R^5 = halogen with a Grignard compound of the formula III

$$R^5\text{-}MgX \qquad (III),$$

in which R^5 has the abovementioned meaning and X is halogen, in the presence of nickel-phosphine complexes.

4. A fungicidal agent which contains an effective amount of a compound of the formula I as claimed in claim 1 or 2.

5. The use of compounds of the formula I as claimed in claim 1 or 2 for controlling harmful fungi.

6. A method for controlling harmful fungi which comprises applying an effective amount of a compound of the formula I as claimed in claim 1 or 2 to the plants, surfaces or substrates attacked by them.

Fetherstonhaugh & Co.
Ottawa, Canada
Patent Agents